Photon energy dependence of the laser-induced emission yield of Si atoms from the Si(100) 2×1 surface

1996 J. Phys.: Condens. Matter 8 1475

(http://iopscience.iop.org/0953-8984/8/10/017)

J. Phys.: Condens. Matter **8** (1996) 1475–1484. Printed in the UK

Photon energy dependence of the laser-induced emission yield of Si atoms from the Si(100) 2×1 surface

In-Keun Yu, Jun'ichi Kanasaki, Akiko Okano†, Yasuo Nakai‡ and Noriaki Itoh§

Department of Physics, Faculty of Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-01, Japan

Received 5 September 1995, in final form 30 October 1995

Abstract. We have carried out measurements of the temperature dependence of the emission yield of Si atoms from the Si(100) 2×1 surfaces induced by nanosecond laser pulses of several photon energies. The yield is plotted as a function of $E = h\nu - E_G(T)$, where $h\nu$ is the photon energy and $E_G(T)$ is the band-gap energy at temperature T where the yield is measured. We find that the Si emission yield is within the noise level for $E = 0.9$–1.15 eV (region I), increases to a saturation level for $E = 1.15$–1.42 eV (region II) and increases further for $E = 1.42$–2.15 eV (region III). The results are compared with those for GaP, GaAs and InP.

1. Introduction

Recent measurements of laser-induced atomic emissions with submonolayer sensitivity have demonstrated defect-initiated atomic emissions from semiconductor surfaces, such as Si, GaAs, GaP and InP [1]. The yield has been found to change as irradiation is repeated on the same spot of the surface in a fluence range at which irradiation induces no change in the low-energy electron diffraction (LEED) pattern [2]. This result has been interpreted to indicate that the emission is originated from defect sites on surfaces. The yield is a superlinear function of laser fluence [2]. The measurements of the excitation spectra in the laser fluence range where no destruction of the LEED pattern is observed have shown that the emission is entirely of electronic origin. These results imply that electronic excitation leads to bond breaking of atoms associated with defects on the surfaces. Several defect types can be differentiated from measurements of the yield change by repeated irradiation on the same spot; the yield originating from adatom-type defects is reduced rapidly (A component), that originating from step-type defects is reduced slowly (S component) and that originating from vacancy-type defects increases (D component), as irradiation on the same spot is repeated. Because of the superlinear dependence of the yield on laser fluence, the threshold laser fluence for each component of emission can be defined. The threshold laser fluence is the lowest for component A, and it is higher for S and D components in that order [3]. The threshold laser fluence for the D component is designated as F_D.

† Present address: Takayanagi Particle Surface Project, ERATO JRDC, JEOL Ltd., 3-1-2 Musasino, Akishima, Tokyo 196, Japan.

‡ Present address: Department of Electrical Engineering, Daido Institute of Technology, 2-21 Daido-cho, Minami-ku, Nagoya 457, Japan.

§ Present address: Department of Physics, Osaka Institute of Technology, 16-1 Omiya 5-Chome, Asahi-ku, Osaka 535, Japan.

0953-8984/96/101475+10$19.50

Irradiation above the threshold laser fluence F_D for the vacancy-initiated emission leads to destruction of the LEED pattern of the original reconstructed structure. Thus, F_D can be regarded as the laser ablation threshold as detected by LEED observation [2]. It has been shown that F_D for GaP and GaAs shows a photon-energy dependence almost the same as the macroscopic ablation laser fluence [1]. Thus, it is suggested that the bond breaking that induces submonolayer atomic emissions is responsible for laser ablation.

The phenomenon of laser-induced atomic emissions is of basic interest [1]. The superlinear yield–fluence relation suggests that single excitation does not result in emissions. This result can be easily understood, because the energy required to break the bond of even an adatom on these semiconductor surfaces is larger than the band-gap energy. For example, the antibonding state for an adatom on a Si surface is within the continuum [4]. Photons with energies not much higher than the band-gap energy create energetic electrons and holes, which relax by emitting phonons to the bottom of the conduction band and to the top of the valence band, respectively. Thus, unless the energy transfer from highly excited electron–hole pairs to the antibonding state is effective as in metal–adsorbates systems [5], single excitation cannot lead to emissions. The superlinear yield–fluence relation suggests multiple excitation or high-density excitation to be the cause of emissions.

Several mechanisms have been invoked to explain the laser-induced emissions. Itoh and Nakayama [6] have suggested that atomic emissions can be induced by localization of two holes by virtue of lattice deformation that finally leads to removal of an atom from the surface. According to their original suggestion, the potential barrier for reaching the two-hole localized state is overcome because of the screening of Coulombic repulsion in a dense electron–hole plasma. It has been suggested by Sumi [7] that a potential barrier can be surpassed in a dense electron–hole plasma because of the degeneracy of the valence band. Pankratov and Scheffler [8] have shown that localization of two excitons on surfaces can be the cause of the atomic emissions. Hattori *et al* [9] have suggested that the cascade excitation of defect sites, accompanied by lattice relaxation after each excitation, is the cause of the emissions.

The laser-induced atomic emissions described above do not involve core excitation. Thus, the mechanism of emissions by intense laser irradiation is different from that induced by core excitation, by which localized two holes in the valence band are generated within 1 fs [10]. The mechanism of laser-induced emissions described above involves electron–lattice interaction. Anderson [11] suggested that two-hole localization can occur if the Coulomb repulsion energy E_{Coul} due to on-site localization of two holes is smaller than the lattice relaxation energy E_{LR} gained by the localization (called negative U; $U = E_{Coul} - E_{LR}$). Like the two-hole localization resulting from core excitation, localization of two holes on the bonding orbital for a specific atom on surfaces can weaken the bond and lead to atomic emissions [12].

One experimental clue for understanding the mechanism may be obtained from spectroscopic studies. Measurements of the photon energy dependences of the emission yield mainly originating from step-type defects have been carried out for GaAs(110) [13, 14], InP(110) [15] and GaP(110) [16, 17] surfaces. In these measurements, the temperature dependence of the yield was measured at several photon energies, and the yield was plotted as a function of $E = h\nu - E_G(T)$, where $E_G(T)$ is the bulk band-gap energy at temperature T, where the yield is measured. It has been shown that the direct band-gap semiconductors GaAs and InP behave similarly to each other; a sharp drop in the emission yield to the noise level is observed at nearly 100 meV below the band-gap energy and the yield is recovered as the photon energy crosses the band-gap energy. A similar reduction occurs in GaP, an indirect semiconductor, but the yield does not recover for about 1.5 eV above the band-gap

energy. The reduction has been ascribed to resonant energy transfer from the excited state of a surface defect to the bulk exciton. For GaAs, a further increase in the emission yield has been observed at photon energies at which the excitations of electrons of the occupied surface states become feasible, one to the bulk conduction band and the other to the surface unoccupied states. The relevance of the increases in the yield to the transitions involving the surface occupied state has been shown using polarization measurements; the yield is higher when the electric vector of the incoming laser beam is polarized along the Ga–As chain on the (110) surface.

To make clear the mechanisms of the defect-initiated laser-induced atomic emissions, it is of particular interest to extend spectroscopic data to another indirect-band-gap semiconductor. The purpose of the present paper is to report the experimental observation of the excitation spectroscopy of laser-induced atomic emission from the Si(100) 2×1 surfaces, for which the atomic [18] and electronic [19] structures have been well documented. For detailed spectroscopic measurements, we followed the previous procedures [16] for obtaining excitation spectra: change the temperature and laser photon energy and plot the yield as a function of E.

2. Experimental technique

A sample of p-type Si(100) of 5 mm $\times$ 15 mm $\times$ 0.3 mm size was mounted on a sample holder in an ultra-high-vacuum chamber. The chamber is equipped with facilities for Auger electron spectroscopy (AES) and LEED and was evacuated to 10^{-11} Torr. Clean Si(100) surfaces were prepared by annealing at 970 K for 20 h [20]. In obtaining the excitation spectra, the specimen was heated at several temperatures between 300 and 700 K. Heating was performed using a tungsten filament attached to the sample holder, and the temperature was measured using a chromel–alumel thermocouple.

The cleaned Si(100) surface was irradiated with 28 ns laser pulses generated with an excimer-pumped dye laser. Two data points for ablation threshold at $E = -0.124$ ($h\nu = 0.956$ eV) and 0.25 eV ($h\nu = 1.33$ eV) were obtained using 10 ns laser pulses generated with an optical parametric oscillator system pumped with the 355 nm third harmonic of a Nd: YAG laser. Si atoms were resonantly excited and then ionized using another pulsed laser beam generated from another excimer-pumped dye laser. The photon energy of this laser beam is the same as the $^3P_0$–$^3P_1$ transition energy (4.928 eV) of a Si atom. Ionized Si atoms were detected with a microchannel plate. Each time that the dye was changed, the size of the laser beam for inducing emissions, typically 0.3 mm, was estimated from images on photographic films and by measuring transmission through a slit with variable width. Further details of the experimental technique have been described elsewhere [9].

3. Experimental results

The yield Y versus E relation for the Si(100) 2×1 surface was obtained in the following way. Starting from the lowest fluence available, we irradiated a surface spot with increasingly higher fluence at room temperature, until the rapidly decaying component was eliminated. Then the temperature dependence of the yield was measured between room temperature and 700 K. After cooling to room temperature, a new experimental run was done at another photon energy. In changing the photon energy, we adjusted the grating for the wavelength selector or changed dyes. When the wavelength is changed, the specimen was shifted

slightly so that a new surface spot is irradiated with a laser beam of new photon energy. These processes were repeated for photon energies between 2.07 and 3.26 eV.

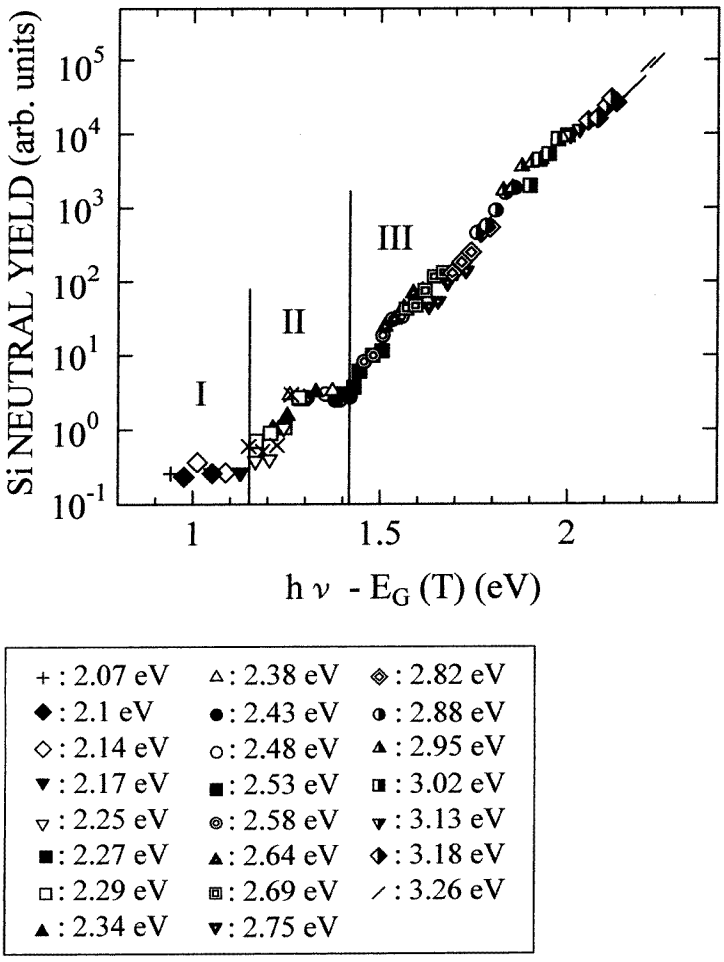

Figure 1. (a) The photon energy dependence of Si^0 emission yield from the Si(100) 2×1 surface as a function of $E = h\nu - E_G(T)$, where $h\nu$ is the photon energy and $E_G(T)$ is the band-gap energy at temperature T. The data points include the yield versus temperature relation obtained with several values of $h\nu$, indicated in (b).

The Y–E relation was obtained by plotting all experimental data as a function of $E = h\nu - E_G(T)$. The result is shown in figure 1. $E_G(T)$ obtained experimentally by Jellison *et al* [21] was used. In obtaining figure 1(a), multiplication factors were applied to the yield so that the Y–E relation falls into a single curve. This process compensates the error mainly arising from the measurement of fluence or of the area of laser beams. The factors used were in the range 2-4. The fact that data points obtained with different photon energies overlap each other assures that the method used at present is appropriate. The procedure makes is possible to obtain the Y–E relation over a large dynamic range, although an appropriate range of laser fluences was chosen for each photon energy so that the number of emitted atoms is within the dynamic range of the detector.

For convenience we divide the Y–E relation into three regions: region I, $E = 0.9$–1.15 eV; region II, $E = 1.15$–1.42 eV; region III, $E = 1.42$–2.15 eV. In region I, the emission yield is within the noise level. We have carried out measurements for energies as low as $E = 0.3$ eV, but no appreciable emission was obtained. The yield is found to increase to a saturation value in region II. In figure 2(a), we plot the temperature dependences obtained with several photon energies in region II. Figure 2(b) shows detailed Y–E plots in this region. In region III, Y increases continuously as the photon energy increases. Further details of the temperature dependence in region III are shown in figure 3. Evidently, the Y–T relations for several photon energies are nearly parallel, showing that the increase is continuous.

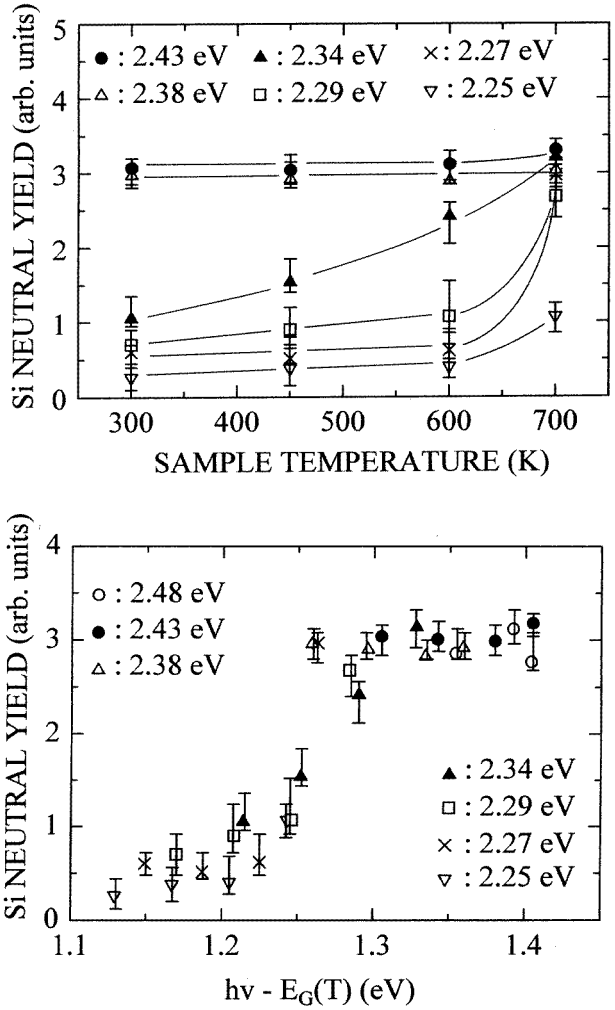

Figure 2. (a) The temperature dependences of the Si^0 emission yield from the Si(100) surface induced by laser pulses of several photon energies indicated in the figure. (b) A replot of (a) showing the relation between yield and $E = h\nu - E_G(T)$ for region II.

Typical yield versus fluence relations for regions I, II and III are shown in figure 4. Taking into account the noise level of the detector, we determined the threshold laser fluence

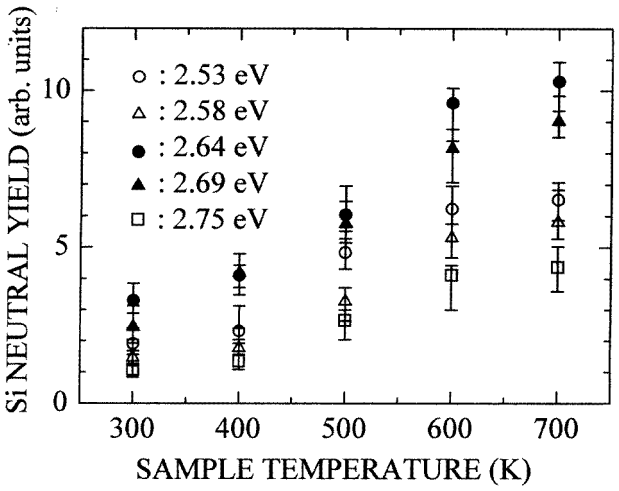

Figure 3. The temperature dependences of the Si^0 emission yield from the Si(100) surface induced by laser pulses of several photon energies (region III) indicated in the figure.

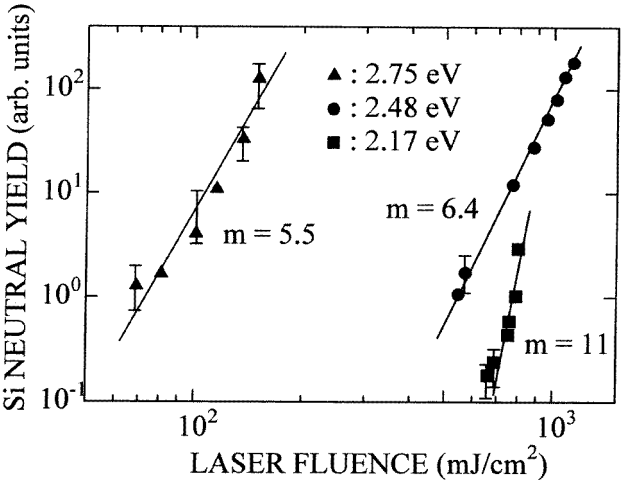

Figure 4. The laser fluence dependences of the Si^0 emission yield from the Si(100) surface induced by laser pulses of 2.17 eV (region I), 2.48 eV (region II) and 2.75 eV (region II). The power indices are $m = 11$, 6.4 and 5.5 for regions I, II and III, respectively.

for 2.17 eV, 2.48 eV and 2.75 eV photons as 650 mJ cm^{-2}, 510 mJ cm^{-2} and 70 mJ cm^{-2}, respectively. For 2.17 eV photons (region I), the yield is extremely small for laser fluences lower than 0.7 J cm^{-2}. An extremely rapid increase observed above this laser fluence is typical for the yield–fluence relations above F_D [1]. Thus, it appears that no emission due to components A and S is observed in this energy range, as is the case for GaP, another indirect-band-gap semiconductor. Relatively moderate yield–fluence relations are observed for other photon energies, with the power indices 5–6. These values are typical for components A and S [1, 22]. The threshold laser fluence for 2.75 eV photons (region III) is much lower than those for 2.48 eV (region II) and 2.17 eV photons. This result explains the orders-of-magnitude increase in the yield as E increases, as shown in figure 1, which

plots the results for laser fluences of approximately $0.7F_D$.

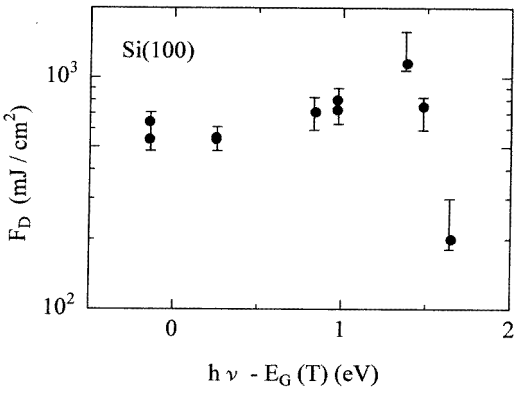

Figure 5. The dependence of F_D, the laser fluence above which yield–fluence relations with a high power index starts, on $E = h\nu - E_G(T)$.

We measure the laser fluence F_D at which the yield–fluence relation of high power index starts for several photon energies. The results are shown in figure 5. The results for $E = -0.124$ and 0.25 eV were obtained with laser beams of different characteristics. Therefore these values cannot be directly compared with the other data point. We note that there is no change in F_D when the photon energy crosses the band-gap energy. The ablation laser fluence for $h\nu - E_G(T) < 1.42$ eV (region I and II) is almost constant and it decreases as the photon energy increases to region III. A similar correlation between the decrease in F_D and the increase in the yield has been observed for GaAs [17].

4. Discussion

According to the present spectroscopic studies of laser-induced emissions, the photon energy dependence of the defect-initiated emission yield of Si atoms from the Si(100) surface can be divided into three ranges: I, II and III. In region I, the emission yield is extremely small; a similar low-yield region has been observed for the GaP(110) surface [17]. For GaP, laser-induced emissions are observed for photons of sub-band-gap energies and the yield is diminished at 60 meV below the band-gap energy. No increase in the yield of GaP for photons above the band-gap energy has been detected for $E < 1$ eV. Suppression of the yield has been observed also for the direct-band-gap semiconductors GaAs [14] and InP [15], but the emission yield has nearly recovered at $E = 0$. The atomic emissions observed by photons below F_D should be electronic effects, since they are observed at fluences much smaller than the ablation threshold.

In region II, the yield shows a small stepwise increase followed by saturation. If the factor that suppresses the emission yield in region I is removed, we expect the yield to recover, i.e. to increase and then to saturate. Such an increase followed by saturation has been observed for the GaAs and InP(110) surfaces, for which the suppression of the yield is limited only below the band-gap energy. Thus we consider that the suppression of the emission yield of Si atoms is removed at $E \simeq 1.15$ eV. The onset of the increase in the yield coincides with the conduction band minimum at the L point. As we shall explain later, only the excitation localized on the surface can efficiently lead to atomic emissions but that delocalized to the bulk cannot. Thus we consider that this coincidence is accidental.

We found that the Si^0 yield is extremely small above the band-gap energy for $E < 1.15$ eV. It has been shown that the Ga^0 yield from the GaP(110) surface is also extremely small between $E = 0.1$ eV and $E = 1$ eV, above which no measurement has been made. Yield reductions have been observed for GaAs(110) [14] and InP(110) [15] but are limited to sub-band-gap energy. Thus it appears that the reduction in the yield ranging to more than 1 eV above the band-gap energy is a characteristic of the indirect-band-gap semiconductors. Spectroscopic measurements for GaP have not been carried out to the range where an increase in the yield is observed. However, the present results for the Si(100) surface indicate clearly that the reduction is within a limited energy range above the band-gap energy. The difference between direct- and indirect-band-gap semiconductors has been ascribed to the difference between the optical absorption bands due to excitons bound to surface defects, the energy acceptor of the resonance energy transfer [23]. Although the optical absorption band due to excitons localized on defect sites is of resonance type in direct-band-gap semiconductors, that for indirect-band-gap semiconductors is known to have a tail extending over the band edge [24]. According to Dexter [25], the resonant energy transfer rate is high in the photon energy range where the optical absorption bands for the energy donor and acceptor overlap. Thus, the resonant energy transfer from a defect excited state, which is considered to have a broad optical absorption band due to the transitions to the resonant state embedded in continuum, extends over a wide energy range in indirect-band-gap semiconductors. Thus the present results support the interpretation that the reduction is due to the energy transfer.

The increase in the yield in region III for the Si(100) surface is analogous to the similar increase for GaAs at 0.45 and 1.10 eV above the band-gap energy. For GaAs the increase is ascribed to the onset of the optical transitions from the surface occupied state to the bulk conduction band and to the surface unoccupied state. For Si, the occupied surface state originating from the dangling bonds is located 0.3 eV below the top of the valence band and the surface unoccupied state starts from the bottom of the conduction band [19, 26]. Thus, the transitions from the top of the surface occupied state to the bulk conduction band and surface unoccupied state occur in the energy range where the emission yield is extremely low. We consider that the enhancement that is effective in GaAs does not work for the Si(100) surface because the reduction due to the energy transfer to the bulk exciton exceeds the enhancement. According to theoretical calculation due to Pollmann *et al* [27] and experimental results obtained by Johansson *et al* [28], the bonding orbital of the dimer bonds appears between 1.3 and 3.5 eV below the top of the valence band. The increase in the yield may be ascribed to the onset of the transitions from this band to the bulk conduction band or to the surface unoccupied state.

The mechanism of the contribution of holes in the surface occupied state to atomic emissions is not yet clear. Conceivable mechanisms are firstly that the onset of the transitions involving the surface occupied states increases the number of electron–hole pairs localized on the surface and the probability of creating two-hole localization increases and secondly that the transition probability in a defect is enhanced due to resonant coupling with the surface transitions.

The photon energy dependence of F_D is similar to the results for other semiconductors; F_D shows little photon energy dependence near the band-gap energy and decreases in the energy range where the emission yield below F_D increases. Thus it appears that the laser ablation detected by high-sensitivity measurements occurs by the mechanism that is responsible for the defect-initiated atomic emissions. It has been pointed out the emissions of weakly bonded atoms around surface vacancies are the cause of ablation [17, 29]. The present experimental observation is in accordance with the previous interpretation. The

possibility that the photon energy dependence of F_D represents that of the melt threshold cannot be entirely excluded. However, the absence of the photon energy dependence upon crossing the band-gap energy suggests that the mechanisms of the emissions leading to the loss of the surface LEED pattern by photons below and above the band-gap energy are the same, at least near the band-gap energy.

Recent observations by scanning tunnelling microscopy (STM) of the Si(100) surface have revealed a variety of defects, including steps and missing atoms [18, 30, 31]. As for GaAs and GaP surfaces, we consider that the emissions below F_D arise from steps. The emissions above F_D appear to occur by vacancies or missing atoms. Indeed single and double missing dimers, called type A and type B defects, have been found by STM observation. It has been shown recently [31] that the so-called type C defects play a role in buckling the dimers on the surface. These defects are misarranged dimers and are considered to be bonded fourfold. Thus, we consider that the threshold laser fluence for the emissions originating from type C defects is higher than F_D [1, 29]. Studies of the change in defect morphology by laser irradiation are needed to elucidate further bond breaking associated with specific defects. A study in this direction has been done for the Si(111) 7×7 surface [32].

In conclusion, the present results show that the excitation spectrum for atomic emissions observed for the Si(100) 2×1 surface is consistent with the results observed in other semiconductors. The presence of a low-yield region is observed until 1.42 eV from the band-gap energy and an increase in the yield accompanied with the reduction in F_D at higher energies is observed. The result that the low-yield region extends more than 1 eV from the band-gap energy appears to be the characteristic of the indirect-band-gap semiconductors. The increase in the yield and decrease in F_D are considered to be related to the transitions involving the surface states.

References

[1] Itoh N, Kanasaki J, Okano A and Nakai Y 1995 *Ann. Rev. Mater. Sci.* **25** 97
[2] Hattori K, Okano A, Nakai Y, Itoh N and Haglund R F Jr 1991 *J. Phys.: Condens. Matter* **3** 7001
[3] Kanasaki J, Okano A, Nakai Y and Itoh N 1994 *Appl. Surf. Sci.* **79–80** 100
[4] Khoo G S, Itoh N and Ong C K 1995 *J. Phys.: Condens. Matter* **7** 2051
[5] Gadzuk J W 1991 *Phys. Rev.* B **44** 13 466
[6] Itoh N and Nakayama T 1982 *Phys. Lett.* **92A** 471
[7] Sumi H 1991 *Surf. Sci.* **248** 382
[8] Pankratov O and Scheffler M 1995 *Phys. Rev. Lett.* **75** 701
[9] Hattori K, Okano A, Nakai Y and Itoh N 1992 *Phys. Rev.* B **45** 8424
[10] Knotek M L and Feibelman P J 1978 *Phys. Rev. Lett.* **40** 964
[11] Anderson P W 1975 *Phys. Rev. Lett.* **34** 953
[12] Ramaker D E, Madey T E, Kurtz R L and Sambe H 1988 *Phys. Rev.* B **38** 2099
[13] Kanasaki J, Okano A, Ishikawa K, Nakai Y and Itoh N 1993 *Phys. Rev. Lett.* **70** 2495
[14] Kanasaki J, Okano A, Ishikawa K, Nakai Y and Itoh N 1993 *J. Phys.: Condens. Matter* **5** 6497
[15] Okano A, Kanasaki J, Nakai Y and Itoh N unpublished
[16] Okano A, Hattori K, Nakai Y and Itoh N 1991 *Surf. Sci. Lett.* **258** L671
[17] Okano A, Kanasaki J, Nakai Y and Itoh N 1994 *J. Phys.: Condens. Matter* **6** 2697
[18] Hamers R J, Tromp R M and Demuth J E 1986 *Phys. Rev.* B **34** 5343
[19] Ortega J E and Himpsel F J 1993 *Phys. Rev.* B **47** 2130
[20] The sample was cleaned by degassing at 970 K about 20 h and then flashed to 1440 K for 2 min to remove the oxide layer. The sample was gradually cooled at a speed of 0.5 K s^{-1} to room temperature.
[21] Jellison G E Jr and Modine F A 1983 *Phys. Rev.* B **27** 7466
[22] Kanasaki J, Yu I-K, Nakai Y and Itoh N 1993 *Japan. J. Appl. Phys.* **32** L859
[23] Singh J, Itoh N, Nakai Y, Kanasaki J and Okano A 1994 *Phys. Rev.* B **50** 11 730
[24] Faulkner R A 1968 *Phys. Rev.* **175** 991

[25] Dexter D L 1953 *J. Chem. Phys.* **21** 836
[26] Himpsel F J and Eastman D E 1979 *J. Vac. Sci. Technol.* **16** 1302
[27] Pollmann J, Kruger P and Mazur A 1987 *J. Vac. Sci. Technol.* B **5** 945
[28] Johansson L S O, Uhrberg R I G, Martensson P and Hansson G V 1990 *Phys. Rev.* B **42** 1305
[29] Itoh N, Okano A, Hattori K, Kanasaki J and Nakai Y 1993 *Nucl. Instrum. Methods* B **82** 310
[30] Wolkow R A 1992 *Phys. Rev. Lett.* **68** 2636
[31] Tochihara H, Amakusa T and Iwatsuki M 1994 *Phys. Rev.* B **50** 12 262
[32] Ishikawa K, Kanasaki J, Nakai Y and Itoh N 1996 *Surf. Sci. Lett.* at press